

Temperature variation of the lattice constant and the coefficient of thermal expansion of ammonium chloride

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Using an extrapolation technique as well as Cohens least square method, precision determination of the lattice constant of ammonium chloride has been made at different temperatures between 20–245°C. From these, by a graphical treatment, the coefficients of thermal expansion at various temperatures have been evaluated. The transformation characteristic of ammonium chloride from α - β form around 185°C has been studied by high temperature X-ray diffraction techniques.

1 INTRODUCTION

The effect of temperature of ammonium chloride has been the subject of numerous discussions. According to Wallace (1910) there is a marked change in the heat effect of ammonium chloride (NH_4Cl) at 159°C. Scheffer (1916) finds that Wallace's result is too low, for the transition temperature is 184.5°C. Hachmeister (1919) gave 174°C for the transition temperature of NH_4Cl from $\alpha \rightarrow \beta$ and Bridgman (1916) gave 184.3°C. Wegscheider (1908, 1911) postulated that NH_4Cl is stable and is transformed at 184.5°C into β NH_4Cl in the presence of moisture but that sometimes a labile α' form is produced which evaporated without dissociation. In view of the discrepancies in these results an accurate redetermination of transition temperature was thought to be worthwhile.

Ammonium chloride belongs to the cubic system. Further, NBS circular (1953) reported the length of the unit cell of NH_4Cl as 3.8756 Å at 26°C. Bartlett & Langmuir (1921) gave the lattice constant as 6.533 Å at 250°C. Data on the linear coefficient of thermal expansion of this salt has been reported by Fizeau (1867) as 62.546×10^{-6} at 40°C. Nevertheless, extensive X-ray determination of the coefficient of thermal expansion over a wide range of temperature has not so far been reported. The present paper reports an accurate redetermination of the transition temperature of NH_4Cl from $\alpha \rightarrow \beta$ form and the coefficient of thermal expansion over the range of temperature 20–165°C. It was felt that such an investigation might throw some light on the physical characteristics such as caking, of the complex mixed fertilizers containing NH_4Cl .

2. EXPERIMENTAL

Transition temperature

Phase transformation studies of NH_4Cl has been done over the range of temperature 20–245°C, by X-ray powder diffraction method in Guinier-Lenne High Temperature X-ray Camera. The special feature of this camera is that by means of a synchronously moving film cassette with continuous monitoring of the temperature, structural changes of a system are investigated by recording the characteristic X-ray diffraction lines.

From the X-ray diffraction pattern obtained by the above technique, it has been found that the transformation of NH_4Cl from α to β form takes place around 185°C. This corroborates the results obtained by Scheffer (1916) and Smith *et al* (1915, 1919) who reported that the transformation α - β form occurs at this temperature. However, in one of the diffraction photographs (Figure 1) taken in Guinier-Lenne High Temperature X-ray Camera, the sample being kept under vacuum and heated from room temperature to 250°C, it has been observed that α NH_4Cl did not transform to β form. Instead, an additional phase started appearing at 50°C and the formation of this new phase completed at 125°C with the disappearance of α - NH_4Cl (X-ray data is given in table 1). According to

Table 1. X-ray diffraction data for α , β and supposed α' forms of ammonium chloride

$\alpha\text{NH}_4\text{Cl}$		$\beta\text{NH}_4\text{Cl}$		$\alpha'\text{NH}_4\text{Cl}$	
dA	I	dA	I	dA	I
3.876	s	3.285	vs	2.48	w
2.747	vs	2.319	s	2.24	ms
1.93	m	1.98	ms	2.20	m
1.724	mw	1.896	m	1.935	m
1.577	ms	1.643	vw	1.78	w
1.365	w	1.508	vw	1.64	vw
1.284	vw	1.45	w	1.375	mw
1.222	mw	1.343	vw	1.175	m
1.116	vw	1.263	vw		
1.0723	vw	1.176	f		
1.0334	m	etc			
0.9384	vw				
etc.					

Wegscheider (1908, 1911) ordinary α - NH_4Cl being a labile form which changes to α' - NH_4Cl at a higher temperature in the presence of moisture, and it is the transition α' - to β - NH_4Cl which occurs at 184.5°C, while dry α - NH_4Cl does not change. Further, he also postulated that possibly α - NH_4Cl is stable and is transformed at 184.5°C into NH_4Cl , but that sometimes a labile α' -form is produced in the preparation of the salt, and it is this form which evaporates with-

Table 2. Lattice Constant of NH_4Cl at various temperatures

Phase	Temperature	$a(\text{\AA})$
α	20°C	3.8756
	40°C	3.8776
	65°C	3.8793
	85°C	3.8849
	105°C	3.9889
	125°C	3.8965
	145°C	3.9030
	165°C	3.9096
β	—	—
	200°C	6.5375
	225°C	6.5423
	245°C	6.5485

out dissociation. The present experimental evidence for the existence of this unknown phase may be the only proof which can be ascribed to the assumed α' - NH_4Cl because repeated experiments on heating the sample both under vacuum as well as in atmosphere (allowing the sample to absorb moisture) did not give any consistent results. The exact conditions of formation or preparation of this compound is yet to be probed.

3 THERMAL EXPENSION

Lattice constants at room temperature and at elevated temperatures were obtained with the help of 19 cm. dia. cylindrical camera (Unicam). The films recorded six well resolved $\alpha_1\alpha_2$ doublets with CuK_α radiation (Radon House X-ray Unit, 30 KV 16 mA rating). The films were measured on a Philips Comparator with an accuracy of 0.005 cms. Random errors were minimized by repeated measurements. Precision determination of lattice constants were done by Cohens least square method as well as by extrapolation against $\cos^2\theta/\sin\theta + \cos^2\theta/\theta$. The differences in the values obtained by these two different methods were within the experimental errors. Table 2 gives the values of the lattice constants obtained at different temperatures for α - NH_4Cl and its variation corresponding to different temperature is shown in figure 2. From the graph of temperature vs lattice constant, values of a were read at regular intervals of 20°C. From these, the coefficients of expansion at the mean temperature of the interval were derived using the definition

$$\alpha_{20} = \frac{1}{a_{20}} \left(\frac{\Delta a}{\Delta T} \right).$$

By a least squares treatment of the data obtained the following equation was derived for the curve giving the temperature variation of the coefficients of expansion over the range 20–165°C.

$$\alpha_T = 15.47 \times 10^{-6} + 8.243 \times 10^{-8}T + 14.77 \times 10^{-10}T^2 \quad \dots (1)$$

The values of the coefficient of expansion obtained by using the above equation are compared with the values derived using the definition (Table 3). The uncertainties in the evaluation of coefficients of expansion (α_T) is very much reduced in the higher range of temperature.

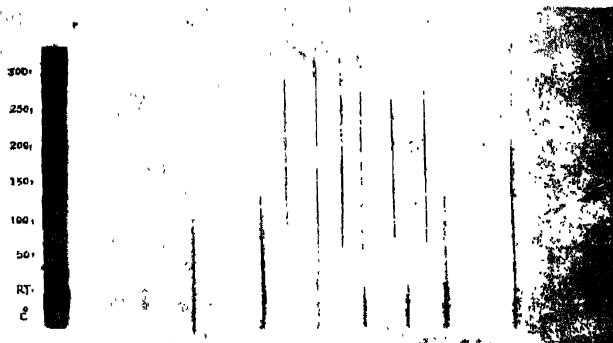


Fig. 1. Guinier-Lenne High temperature X-ray Photograph of ammonium chloride.

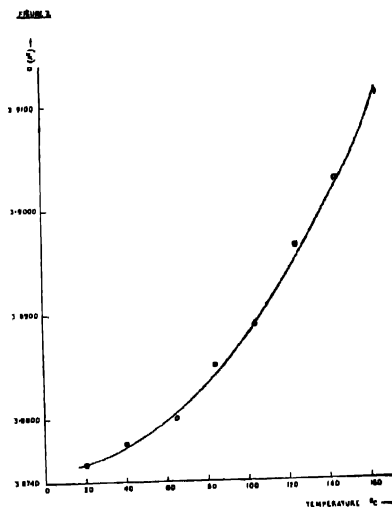


Fig. 2. Plot of lattice constant against temperature.

Table 3. Coefficient of expansion of NH_4Cl at various temperatures

Temperature °C	α from the definition	α from equation (1)	% $\Delta\alpha$
40	20.63×10^{-6}	20.13×10^{-6}	+2.42
60	24.48×10^{-6}	25.13×10^{-6}	-2.66
80	32.51×10^{-6}	31.52×10^{-6}	+3.35
100	39.22×10^{-6}	38.48×10^{-6}	+1.87
120	48.27×10^{-6}	46.63×10^{-6}	+3.39
140	55.96×10^{-6}	55.96×10^{-6}	—
160	65.77×10^{-6}	60.47×10^{-6}	-1.06

Lattice constants obtained at different temperatures varies from 3.8756 Å at 20°C to 3.9096 Å at 165°C for $\alpha\text{-NH}_4\text{Cl}$ and in the case of $\beta\text{-NH}_4\text{Cl}$ it varies from 6.5375 Å at 200°C to 6.5485 Å at 245°C. By inspection of X-ray diffraction data (table 1) it is easily recognizable that α -phase is simple cubic lattice and β -phase is FCC. The measured values for the linear coefficient of expansion for β -phase (FCC) in the range 200–245°C is 37.33×10^{-6} per °C. A rough check of the values of lattice expansion (table 2) shows that the lattice expansion is comparatively greater in β -phase than α -phase suggesting that in a general way, the weakening of the binding forces with the rise of temperature. Further, the fact that expansion coefficient of α -phase is smaller than the expansion coefficient of β -phase may also be understood in terms of the strong intralayer binding in α -phase.

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